QUANTUM CHEMICAL EVALUATION OF COMPLEX FORMATION OF CO (II) IONS WITH QUERCETIN MOLECULE

Arzimurodova X.[1], Ismatov D.M.[1], Uzokov J.R.[1], Mukhamadiyev A.N.[1], Mukhamadiev N.Q.[1], Fattoyeva N.H.[2]

EMAIL: m_nurali@mail.ru

[1]*Samarkand State University. Samarkand, Uzbekistan*
[2]*Samarkand State Institute of Foreign Languages. Samarkand, Uzbekistan*

ABSTRACT: The reactions for the formation of 3- and 5-hydroxyflavanoid chelates from the cations quercetin ($C_{15}H_{10}O_7$) and Co (II) were evaluated by quantum chemical methods. Also, physical parameters such as the stability constant of chelates, the distribution of charge density in the molecule, the activation energy were calculated using the functional theory of density DFT (density functional theory). According to him, the stability constant of the complex formed by the cation Co (II) and flavonoid quercetin $log\beta = 4.56$; the dipole moment of the complex has D = 6,125. The energy of the bonds formed by the quercetin-Co (II) complex at 4C=O and 5-OH is 78,912 kcal/mol, and for the bonds for 3'-OH and 4'-OH, 76,361 kcal/mol. was found to be a commodity.
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KEYWORDS: quercetin, chelate complex, quantum-chemical calculations, DFT, Ab initio, stability constant, dipole moment.

INTRODUCTION

Flavonoids are polyphenolic compounds with many biological and chemical activities, capable of forming flavonoid/metal nanocomposites with metal ions due to carbonyl and hydroxyl groups [1]. The use of complexes formed in the presence of flavonoids and metal ions is due to their properties such as luminescent, anti or prooxidant, antichymolytic. Also, the metabolism and biological activity of flavonoids depend on their configuration, the total number of hydroxyl groups, and the exchange of functional groups in their molecule [2]. Many flavonoids have antioxidant activity, the ability to destroy free radicals, prevent cardiovascular disease, have hepatoprotective, anti-inflammatory and anti-cancer effects, while some flavonoids have potential antiviral effects . In plant systems, flavonoids help fight oxidative stress and act as a growth regulator. With the help of microbial biotechnology for pharmaceutical purposes, it has become possible to mass-produce various flavonoids [3-8].

The formation of flavonoids with ions of intermediate meals (Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}) leads to the formation of new physicochemical properties and biological activities. However, the biological

significance of flavonoid-metal ion complexes has not yet been fully elucidated [9-14]. In addition, there is a lack of information to explain their molecular purpose and mechanisms of action. Therefore, the study of the possibility of complex formation of quercetin with various metal ions is important in terms of obtaining nanoparticles from them. In this study, the ability of quercetin to form complexes with Fe^{2+} ions was quantum-chemically evaluated [15].

The aim of the work is to quantum chemical evaluation of the complex formation of Co (II) ions with a quercetin molecule.

The results obtained and their discussion. The study of the mechanism of reactions of chelate formation from flavonoids and ions of some intermediate metals by quantum chemical methods allows to establish the relationship between "structure-properties" by determining the reaction centers and quantifying them [16- 20]. For this purpose, in this study, the mechanism of formation of a hybrid chelate complex formed from flavonoid quercetin and Co (II) ions, thermodynamic parameters such as stability constant, charge density distribution in the molecule, activation energy, semi-empirical (PM3), Ab initio and DFT studied by quantum chemical methods [4].

The quercetin molecule consists of two aromatic rings (A) and oxygen attached to carbon atoms in the 3, 3 ', 4', 5 and 7 states, as well as a number of OH hydroxyl groups (Figure 1). The distribution of electron densities in a molecule using the TS-DFT method can be seen in Figure 2.
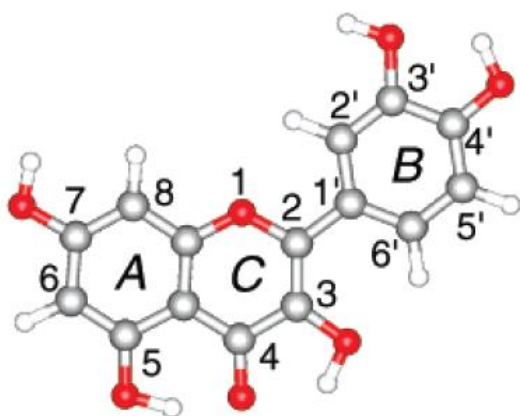

Figure 1. The location of functional groups in the quercetin molecule
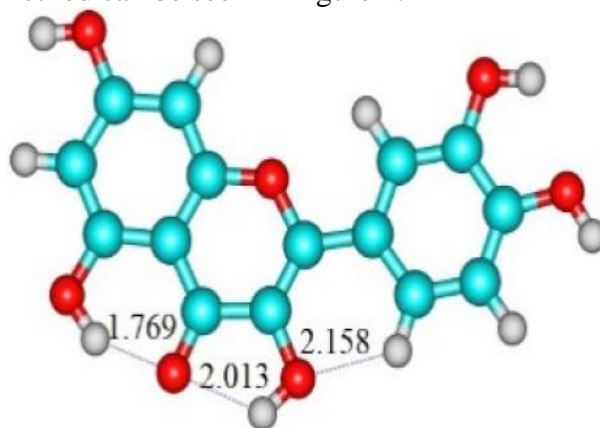

Figure 2. 3.4 and C electron density distribution of a quercetin molecule

The energy of the phenolic-OH bonds in the Quercetin molecule and the electron density distribution in them are important in the formation of metal complexes. The dissociation energies of phenol-OH groups in the quercetin molecule in semi-empirical methods are given in Table 1.

Table 1

The dissociation energy of OH groups in an optimized quercetin molecule

Complex	7-OH	5-OH	3-OH	3'-OH	4'-OH
Quercetin-Fe (II)	14,28	10,12	12,53	15,46	14,02

It can be seen from the table that the dissociation energy of 5-OH and 3-OH hydroxyl bonds is the lowest.

In the formation of a complex between the cation Co (II) and quercetin, the flavonoid is formed due to pentahydroxyls in the aromatic ring (A and C) and in the oxygen heterocyclic ring (C) 3,5,7,3',4' (figure 3).
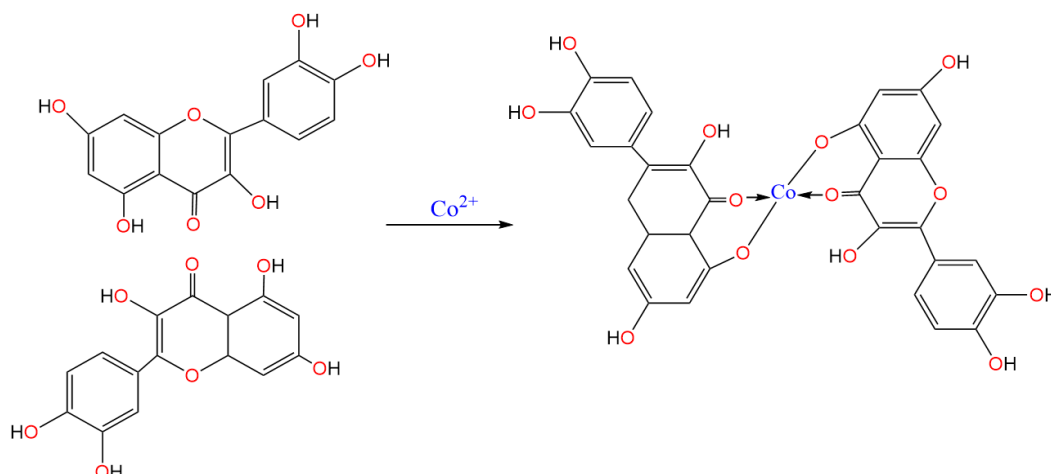
Figure 3. Complex formation

Table 2

Bond energies calculated by the Ab initio method of quercetin and Co (II) cation complexes

Complex	4C=O and 5-OH, kcal/mol	3'-OH and 4'-OH, kcal/mol	3C=O and 5-OH, kcal/mol
Quercetin-Co (II)	78,912	76,361	74,365

From the table, it can be seen that the bonding energy of the functional groups is the lowest at 3C = O and 5-OH. The stability constants of the cation Co (II) and the quercetin complex were calculated by the Mulliken method. It was found that the complex stability constant increases with decreasing garden length. The dissociation energy of the phenolic-OH bond in the flavonoid quercetin molecule was also calculated by quantum chemical calculations (Table 2).

Table 3. Dissociation of finol-OH functional groups in the quercetin molecule

Complex	7-OH	5-OH	3-OH	3'-OH	4'-OH
Quercetin-Co (II)	14,174	26,08	17,40	16,28	14,36

The IR spectra of the complex formed between the cation Co (II) and the quercetin were calculated using the Gaussian 09 program and compared with the experimental IR spectra (Figure 4).
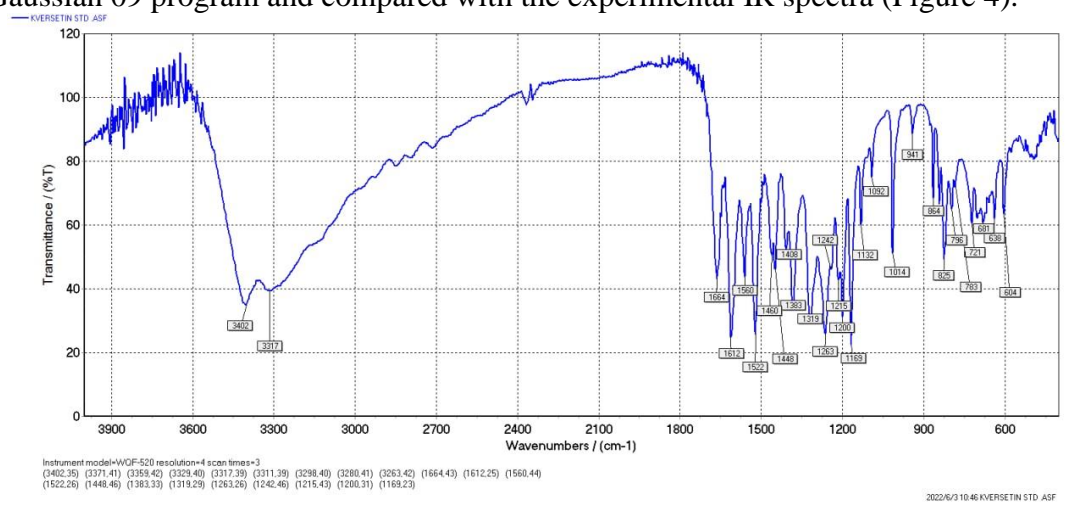

Figure 4. IR spectra obtained as a result of experiments with quercetin

From Figures 4 and 5, the high-intensity peaks in the IR spectra of the complex in the 1600-100 cm^{-1} domains are due to the valence oscillations of the C-H bonds in the aromatic rings, and the peaks in the 3500-300 cm^{-1} domains are due to the differential oscillations of the OH groups. It can be seen that It is also possible to see symmetrical peaks formed in the 400-300 cm^{-1} regions of the spectra due to the deformation oscillations of the Co-O bonds formed by the Co (II) and OH bonds.
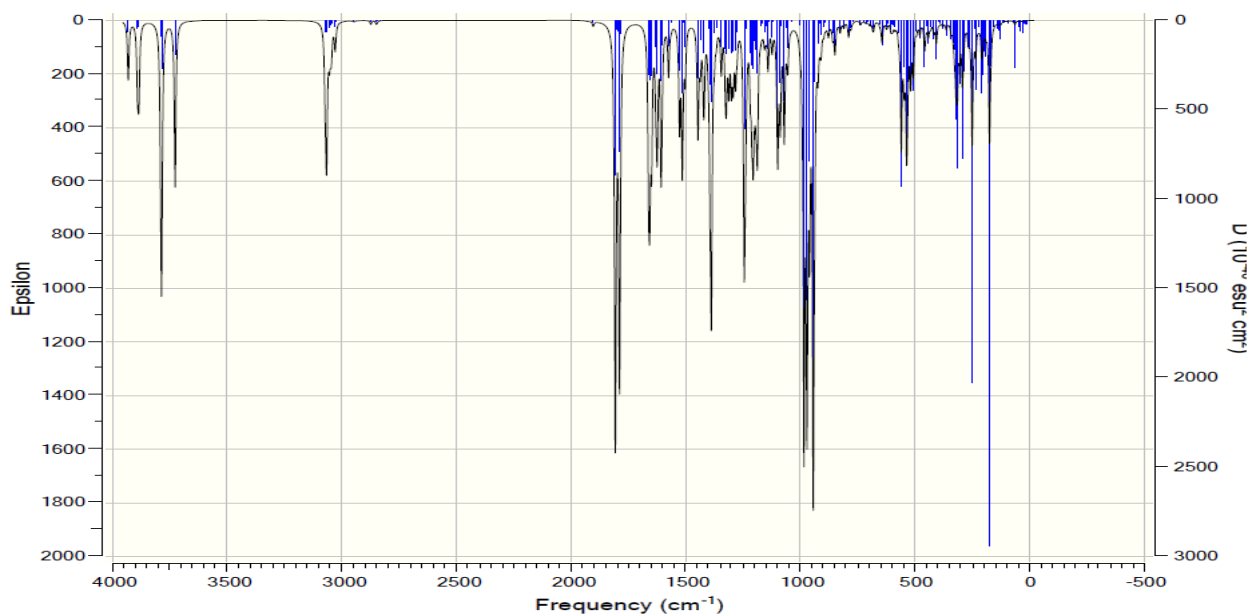

Figure 5. Quercetin and Quercetin-Co (II) complex Gaussian 09
IR spectra calculated in the program

The degree of compatibility of the spectra obtained on the basis of quantum chemical calculations and experiments was evaluated by finding the correlation coefficient by the method of short squares (Figure 6).

As can be seen from Figure 6, the compatibility level of the IR spectra obtained in the experiment and in the Gaussian 09 program was $r^2 = 0.9685$.

In addition, the stability constant of the complex formed between the cation Co (II) and quercetin was determined by DFT. According to him, the stability constant of the chelate formed by the cation Co (II) and two quercetin molecules is $log\beta = 4.56$, and the dipole moment of the quantum chemical molecule calculated by the Mulliken method is 6.125.
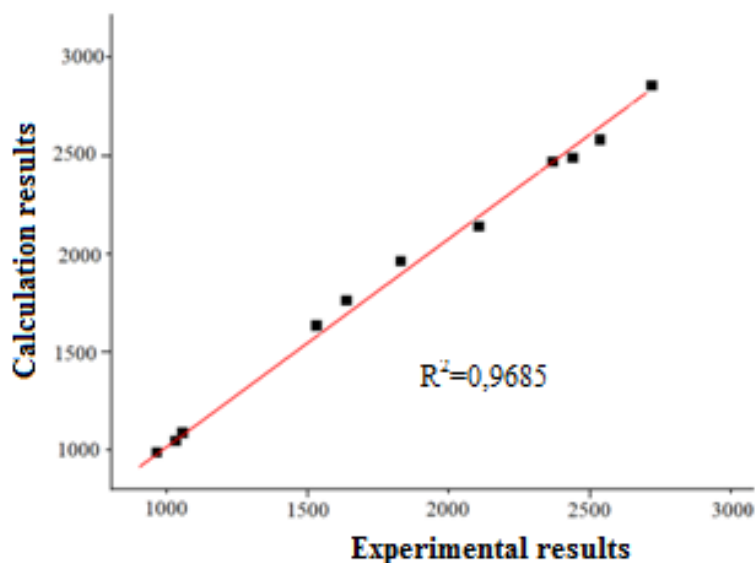
Figure 6. Obtained in the experiment and in the Gaussian 09 program
the degree of compatibility of IR spectra

CONCLUSION

1. The mechanism of formation of hybrid metal / quercetin chelate from quercetin and Co (II) cations, physical parameters such as stability constant, charge density distribution in the molecule, activation energy were evaluated using the functional theory of density DFT (density functional theory).

2. The stability constant of the complex formed from the cation Fe (II) and flavonoid quercetin $log\beta$ = 4.56; the dipole moment of the complex has D = 6,125. The energy of the bonds formed at 4C = O and 5-OH in the Kveretstin-Co (II) complex is 78,912 kcal / mol, and for the bonds 3'-OH and 4'-OH, 76,361 kcal / mol. was found to be a commodity.

3. It was noted that the degree of conformity of the IR spectra of the complex obtained by quantum chemical calculations to the IR spectrum obtained experimentally is r^2 = 0.9685.

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